

12

EUROPEAN PATENT APPLICATION

21 Application number: **90106381.8**

51 Int. Cl.5: **C07C 275/62, D06M 13/432**

22 Date of filing: **12.08.85**

This application was filed on 03 - 04 - 1990 as a divisional application to the application mentioned under INID code 60.

30 Priority: **24.08.84 US 644089**

43 Date of publication of application:
22.08.90 Bulletin 90/34

60 Publication number of the earlier application in accordance with Art.76 EPC: **0 172 717**

84 Designated Contracting States:
AT BE CH DE FR GB IT LI LU NL SE

71 Applicant: **E.I. DU PONT DE NEMOURS AND COMPANY**
1007 Market Street
Wilmington Delaware 19898(US)

72 Inventor: **Pechhold, Engelbert**
111 Harvey Lane
Chadds Ford, Pennsylvania 19317(US)

74 Representative: **Woodcraft, David Charles et al**
BROOKES & MARTIN High Holborn House
52/54 High Holborn
London, WC1V 6SE(GB)

54 **Modified fluorocarbonylimino biurets.**

57 Fluorocarbonylimino biurets derived from a tris(isocyanatoalkane)biuret, a fluoroaliphatic alcohol and a modifier group imports oil/water repellency, soil-release properties.

EP 0 383 365 A2

MODIFIED FLUOROCARBONYLIMINO BIURETS

FIELD OF THE INVENTION

The present invention relates to novel modified fluorocarbonylimino biurets and their use to provide oil/water repellency, soil-release properties.

5

BACKGROUND OF THE ART

U.S. 3,987,227 discloses carpets having a stain-repellent and soil-resistant coating formed by a combination of a water-insoluble fluoroaliphatic radical containing urethane adduct and a water insoluble urethane adduct free from fluoroaliphatic radicals.

U.S. 4,284,484 discloses treating carpets with a combination of:

- (a) a water-insoluble addition polymer derived from polymerizable ethylenically unsaturated monomer; and
- (b) a water-insoluble fluoroaliphatic radical and aliphatic chlorine-containing carboxylic or carbamic ester.

U.S. 4,340,749 discloses treating carpets to render them soil-resistant and stain-repellent with a carboxylic or carbamic ester of a fluoroaliphatic radical- and aliphatic chlorine-containing alcohol.

U.S. 4,401,780 discloses treating textiles with a fluorochemical composition comprising a mixture of:

- (a) a water-insoluble fluoroaliphatic radical and aliphatic chlorine-containing ester;
- (b) a water-insoluble fluoroaliphatic radical-containing polymer; and
- (c) water insoluble fluoroaliphatic radical- containing compound selected from carbonylimino compounds and imine compounds.

Br. 1,241,505 discloses tertiary amine salts of fluorocarbamates which are useful as oil-repellents for treating fabrics.

German Patentschrift 1,794,356 and EPO application 0103752 both disclose various fluorocarbamates having anti-soiling properties.

BACKGROUND AND SUMMARY OF THE INVENTION

The present invention describes novel fluorocompounds which when applied onto fibers and fabrics provide durable finishes with antisoiling properties.

Fluorocarbamates from mono- and diisocyanates have been described previously in various references, such as the references cited above, for improving oil and water resistance of textile surfaces. However, during processing such as washing and drying, a major part of these compounds is lost to the atmosphere and treatment medium, which may cause pollution and operating problems. These problems can be overcome by using reaction products of fluoroalcohols with the biurets of aliphatic or cycloaliphatic isocyanates which give rise to non-volatile and fairly durable textile finishes.

Tris(isocyanato alkane)biurets as used in the invention and their method of preparation are described in U.S. 3,124,605 and 3,201,372. It is believed that the unique biuret structure provides strong hydrogen bonding to the fiber substrate.

Further improvement in durability has been achieved by incorporation of a modifier group (R' or R" below) in the reaction product of fluoroalcohols and tris(isocyanato alkane)biurets. A modifier group may be an aromatic, aliphatic, alicyclic compound or mixture of compounds with one or more Zerevitinov * active hydrogen atoms such as any fluorine-free monomeric alcohol or any substituted or unsubstituted fluorine-containing or fluorine-free diol, triol, tetrol, polyol, amine, diamine, triamine, tetramine, polyamine, hydroxylamine, aminothiols, thiol, dithiol, trithiol, tetrathiol, polythiol, hydroxythiol, carboxythiol; monocarboxylic acid, dicarboxylic acid, tricarboxylic acid, aminocarboxylic acid, etc.

The novel compounds of this invention impart high oil/water repellency and good soil resistance when

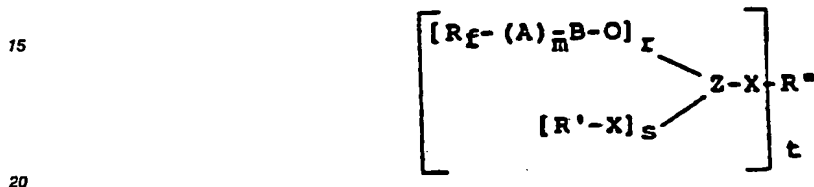
*Zerevitinov determination is the reaction of an organic compound containing active hydrogen atoms, e.g., -OH, -COOH, -NH, etc., with methylmagnesium halide to give methane which is collected and determined volumetrically.

applied onto nylon or polyester fiber or fabric. Similar improvements may be achieved when applied to other synthetic or natural fibers or their blends.

The compounds as described in this invention can be applied onto the substrate pure or in combination with other textile or fluoro-finishes, processing aids, lubricants, anti-stains, etc., either from organic solutions or aqueous dispersions by any of the customary procedures such as spraying, dipping, padding, foaming, etc. The compounds can also be blended with other agents which have oil/water repellency and soil release properties and applied to fibers or fabrics.

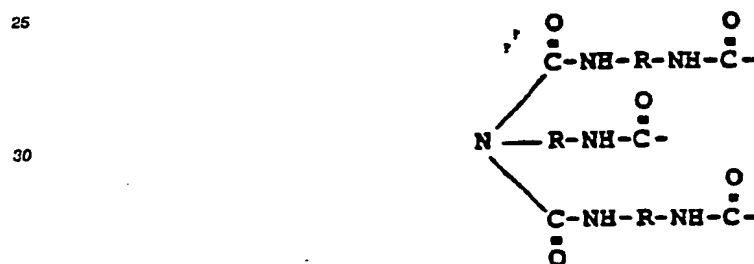
10 DETAILED DESCRIPTION

The novel compounds of the present invention are oligomers of the formula



wherein

Z is a tris(carbonylimino)biuret radical of the general formula



in which R is an aliphatic or cycloaliphatic residue having at least 4 and not more than 20 carbon atoms, with only alkyl, alkoxy or no substituents, especially an alkyl or cycloalkyl residue and most preferably $-(\text{CH}_2)_6-$.

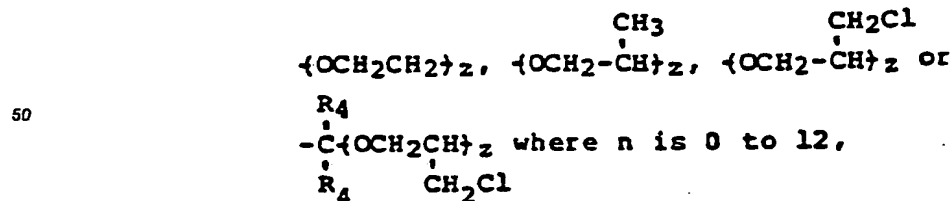
R_f is a fully-fluorinated straight or branched aliphatic radical which can be interrupted by oxygen atoms. Preferably, R_f contains at least 3 and not more than 20 carbon atoms.

A is a divalent radical selected from

$-\text{SO}_2\text{NR}_3-$, $-\text{CONR}_3-$,

where R_3 is H or a C_{1-6} alkyl radical.

B is a divalent linear hydrocarbon radical $-\text{C}_n\text{H}_{2n}-$ which can be end capped by



z is 1 to 50, and R_4 is H or lower alkyl;

X is O, S or NR_5 , where R_5 is H or a lower alkyl;

R'' is any substituted or unsubstituted fluorine-containing or fluorine-free aliphatic, alicyclic, aromatic or

heterocyclic hydrocarbon radical with a valency of at least 2 and not more than 100;

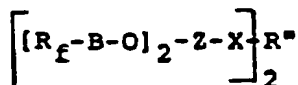
m is zero or 1;

r is 1 or 2;

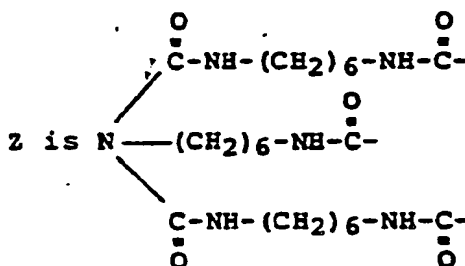
s is (2-r) i.e., either 1 or 0; and

5 t is an integer of 2 to 100.

Preferred compounds include those of the those of the following formula:



wherein



R_f is $-C_nF_{2n+1}$, where n is 3 to 14;

B is $-C_nH_{2n-}$, where n is 2 to 6;

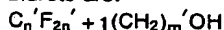
X is O or NH; and

30 R'' is a substituted or unsubstituted fluorine-containing or fluorine-free aliphatic, alicyclic, aromatic or heterocyclic hydrocarbon radical with a valency of 2.

The modified fluorocarbonylimino biurets described in this invention can be prepared by reacting a fluoroalcohol with a stoichiometric excess of a tris(isocyanato alkane)biuret at 50-90° C in the presence of a catalyst such as dibutyltin dilaurate. The amount of catalyst used will depend upon the charge, but is usually only a few drops, e.g., 0.02 to 0.04 parts per mole of reactants. The reaction can be carried out neat or in the presence of a dry solvent such as methyl isobutyl ketone. After 2 to 5 hours reaction is usually complete at which point the free isocyanate (NCO) is determined by the di-n-butylamine titration method. Based on this determination the appropriate amount of modifier is added, to react the residual isocyanate, usually as a solution in an organic solvent such as methyl isobutyl ketone. To allow for completion of the reaction, the mixture is heated for another 8 to 16 hours and then diluted to a 50 to 70 wt % solution with an organic solvent such as methyl isobutyl ketone.

The solution of the modified fluorocarbonylimino biurets can be dispersed in water in the usual fashion by using a surfactant which can be anionic, cationic, or nonionic or a combination of surfactants can be used.

45 Representative fluoroaliphatic alcohols that can be used in the reaction with tris(isocyanato alkane)-biurets are:



where n' is 3 to 14 and m' is 1 to 12;



50 where p' is 1 to 5;

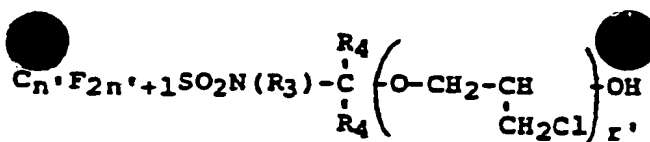


where R_3 is H or lower alkyl, n' is 3 to 14, m' is 1 to 12;



where R_3 , n' and m' are described above;

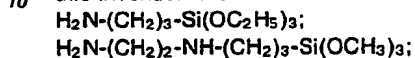
55



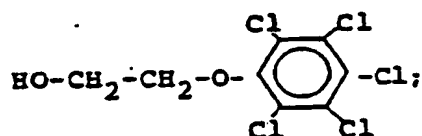
5

where R_3 , n' , m' are described above and R_4 is H or lower alkyl, r' is 1 to 5.

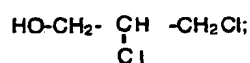
Some of the representative modifiers R' that can be used to make the fluorocarbonylimino biurets of this invention are:



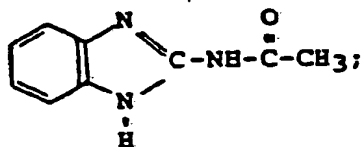
15



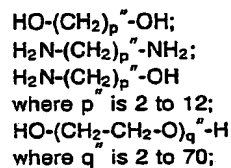
20



25

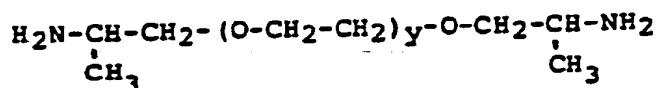


30

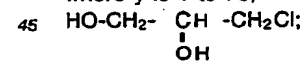


35

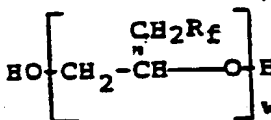
40



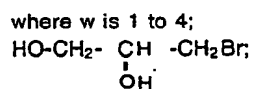
where y is 1 to 70;

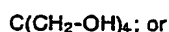
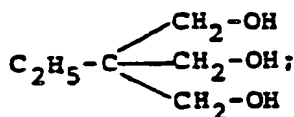
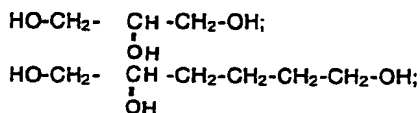
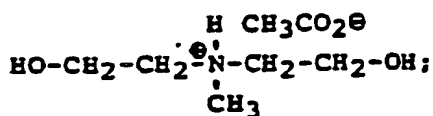
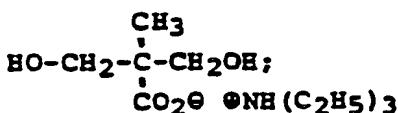
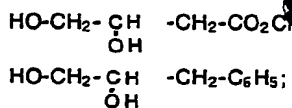


50



55





EXAMPLES

Comparative Example 1

Two moles of a mixture of fluoroalcohols of the formula $F-(CF_2-CF_2)_n-CH_2CH_2OH$ where n' is
45 predominantly 5, 4, and 3, is charged to a reaction vessel and under nitrogen atmosphere heated to 50-
60° C. A 75 wt. % solution of one mole of toluene diisocyanate in methyl isobutyl ketone is added to the
fluoroalcohol and the resulting reaction mixture is agitated and allowed to cool to about 45° C at which point
a catalytic amount of dibutyltin dilaurate (0.02-0.04 g) is added. An exotherm occurs. After the exotherm the
reaction mixture is agitated at 85° C for four hours at which time it is diluted to 67 wt. % solids and allowed
50 to cool.

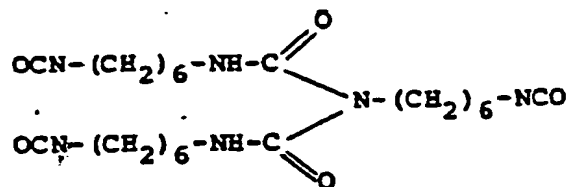
Comparative Example 2

55 Three moles of the fluoroalcohol used in the above example are charged to a reaction vessel and under a nitrogen atmosphere heated to 60-70° C. A 75 wt. % solution of one mole of 1,3,5-tris(6-isocyanatohexyl)-biuret in methyl isobutyl ketone is added to the fluoroalcohol and the resulting reaction mixture is agitated and allowed to cool to about 50° C at which point a catalytic amount of dibutyltin dilaurate is added. An

exotherm occurs. After the exotherm subsides, the reaction mixture is agitated at 60°C for four hours at which time it is diluted to 67 wt. % solids and allowed to cool.

6 Example 1

Two moles of a mixture of fluoroalcohols of the formula $F(CF_2CF_2)_nCH_2CH_2OH$ where n is predominantly 5, 4, and 3, is charged to a reaction vessel and under a nitrogen atmosphere heated to $60^\circ-70^\circ C$. A 75 wt. % solution of one mole of 1,3,5-tris(6-isocyanatohexyl)biuret having the structure



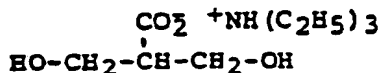
in methyl isobutyl ketone is added to the fluoroalcohol and the resulting reaction mixture is agitated and
20 allowed to cool to about 50°C at which point a catalytic amount of dibutyltin dilaurate is added. An
exotherm occurs. After the exotherm the reaction mixture is agitated at 85°C for three and one half hours,
at which point one half mole of butanediol-1,4 is added. The reaction mixture is heated at 85°C and
agitated an additional 12 hours at which time it is diluted to 67 wt. % solids and allowed to cool.

25 **Example 2**

Two moles of the fluoroalcohol used in Example 1 are charged to a reaction vessel and under a nitrogen atmosphere heated to 60°-70°C. A 75 wt. % solution of one mole of 1,3,5-tris(6-isocyanatohexyl)-biuret in methyl isobutyl ketone is added to the fluoroalcohol and the resulting reaction mixture is agitated and allowed to cool to about 50°C at which point a catalytic amount of dibutyltin dilaurate is added. An exotherm occurs. After the exotherm subsides, the reaction mixture is agitated an additional four hours at 80°C and one third mole of trimethylolpropane $C_2H_5C(CH_2OH)_3$ is added. The reaction mixture is heated at 85°C and agitated for an additional 12 hours at which time it is diluted to 67 wt. % solids with methyl isobutyl ketone and allowed to cool.

Example 3

Two moles of the fluoroalcohol of Example 1 are charged to a reaction vessel and under a nitrogen atmosphere heated to 60°C-70°C. A 75 wt. % solution of one mole of 1,3,5-tris(6-isocyanatohexyl)biuret in methyl isobutyl ketone is added to the fluoroalcohol and the reaction mixture is agitated and allowed to cool to about 50°C at which point a catalytic amount of dibutyltin dilaurate is added. An exotherm occurs. After the exotherm subsides the reaction mixture is agitated an additional four hours at 85°C and one half mole of the triethylamine salt of dimethylolpropionic acid



is added. The reaction mixture is heated at 85° C an additional 12 hours at which time it is diluted to 67 wt. % solids with methyl isobutyl ketone and allowed to cool.

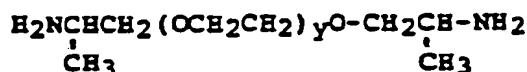
55 Example 4

Two moles of the fluoroalcohol used in Example 1 are charged to a reaction vessel and under a nitrogen atmosphere heated to 60°-70° C. A 75 wt. % solution of one mole of 1,3,5-tris(6-isocyanatoohexyl)-

biuret in methyl isobutyl ketone is added to the fluoroalcohol and the resulting reaction mixture is agitated and allowed to cool to about 50° C at which point a catalytic amount of dibutyltin dilaurate is added. An exotherm occurs. After the exotherm subsides the reaction mixture is agitated an additional three and one half hours at 85° C and one half mole of N-methyl diethanolamine is added. The reaction mixture is heated at 85° C for an additional 12 hours at which time one half mole of acetic acid is added. It is then diluted to 67 wt. % solids with methyl isobutyl ketone and allowed to cool.

Example 5

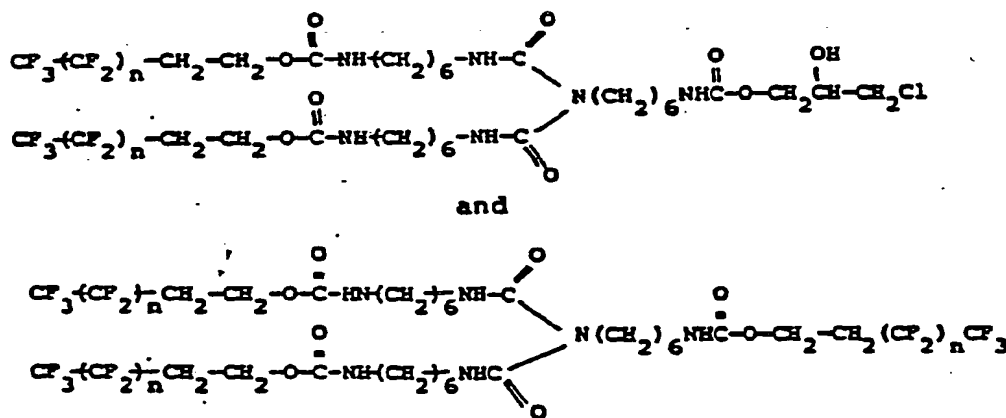
Two moles of the fluoroalcohol used in Example 1 are charged to a reaction vessel and under a nitrogen atmosphere heated to 60°-70° C. A 75 wt. % solution of one mole 1,3,5-tris(6-isocyanatohexyl)-biuret in methyl isobutyl ketone is added to the fluoroalcohol and the resulting reaction mixture is agitated and allowed to cool to about 50° C at which a catalytic amount of dibutyltin dilaurate is added. An exotherm occurs. After the exotherm subsides the reaction mixture is agitated an additional four hours at 85° C and one half mole of polyoxyalkylene diamine such as



where y is 18 is added. The reaction mixture is heated at 85° C and agitated an additional 12 hours at which time it is diluted to 67 wt. % solids and allowed to cool.

Example 6

Two and one half moles of the fluoroalcohol used in Example 1 are charged to a reaction vessel and under a nitrogen atmosphere heated to 60°-70° C. A 75 wt. % solution of one mole of 1,3,5-tris(6-isocyanatohexyl)biuret in methyl isobutyl ketone is added to the fluoroalcohol and the resulting reaction mixture is agitated and allowed to cool to about 50° C at which point a catalytic amount of dibutyltin dilaurate is added. An exotherm occurs. After the exotherm subsides, the reaction mixture is agitated an additional four hours at 85° C and one half mole of 3-chloro-1,2-propanediol is added. The reaction mixture is heated at 85° C and agitated an additional 12 hours at which time it is diluted to 67 wt. % solids with methyl isobutyl ketone and allowed to cool. The product is a mixture which may have the idealized structure shown below:



Example 7

Two moles of the fluorocool used in Example 1 are charged to a reaction vessel and heated to 60°-70° C under a nitrogen atmosphere. A 75 wt. % solution of one mole of 1,3,5-tris(isocyanatohexyl)biuret in methyl isobutyl ketone is added to the fluorocool and the resulting mixture is agitated and allowed to cool to about 50° at which point a catalytic amount of dibutyltin dilaurate is added. An exotherm occurs. After the exotherm subsides, the reaction mixture is agitated an additional four hours at 85° C and one mole of -aminopropyltriethoxysilane $\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$ is added. The reaction mixture is heated at 85° C and agitated an additional 12 hours at which time it is diluted to 67 wt. % solids with methyl isobutyl ketone and allowed to cool.

The stability and durability of the fluorocompounds of this invention are illustrated in Table I. Nylon-66 knit fabric was padded with an aqueous anionic dispersion of the fluorocompounds so as to allow a coverage of about 0.1 wt. % fluorine by weight of dry fabric. The air dried samples were tested for oil and water repellency as described below. Part of the air dried samples were annealed for two minutes in a circulating air oven at 200° C and again tested for oil/water repellency. The above annealed samples were then subjected to five standard home washing cycles and retested.

The home washes were carried out in a "Kenmore" washing machine at 40° C, employing 28 g of "Tide" detergent per washload, followed by drying for 30 minutes in an automatic dryer at medium setting.

Oil and Water-Repellency Tests (Adapted From AATCC Test Method 118)

A piece of fabric, treated with a solution or aqueous dispersion of the polymers of this invention, is conditioned for a minimum of 2 hours at $23 \pm 2^\circ$ and $65 \pm 10\%$ relative humidity. The repellency of carpet samples should be measured on the side of the yarn, not on the tips of the tufts. Beginning with the lowest numbered test liquid (Repellency Rating No. 1), one drop (approximately 5 mm diameter or 0.05-ml volume) is placed on each of three locations at least 5 mm apart. The drops are observed for 10 seconds for the water-repellency test, 30 seconds for the oil-repellency test. If, at the end of those periods of time, two of the three drops are still spherical to hemispherical in shape with no wicking around the drops, three drops of the next higher numbered test liquid are placed on adjacent sites and observed again for the specified periods of time. The procedure is continued until one of the test liquids results in two of the three drops failing to remain spherical or hemispherical, or wetting or wicking occurs. The oil-repellency rating and the water-repellency rating of the yarn, fabric or carpet each is the highest numbered test liquid for which two of three drops remain spherical or hemispherical with no wicking for the specified time.

STANDARD WATER TEST LIQUIDS		
Water-Repellency Rating Number	Composition (Volume %)	
	Isopropanol (Reagent Grade)	Distilled H ₂ O
1	2	98
2	5	95
3	10	90
4	20	80
5	30	70

Dry Soiling Test

Treated and untreated carpets are exposed simultaneously to floor traffic for 10,000 footsteps. They are then removed from the floor and vacuumed. Then a class rating to indicate degree of retained soil is assigned to the treated carpets using the untreated carpet as the basis for comparison.

Wet Soiling Test

A slurry of dirt and water is prepared. A shoe sole is dipped into the slurry and then pressed down in the same manner on each of the treated and untreated carpets to be tested. Following air drying and vacuuming, a class rating is assigned exactly as in Dry Soiling (above).

Scale of Visual Rating	
Rating	Appearance Compared to Control
1 W	Worse
0	Control
1	Slightly Better
2	Better
3	Much Better
4	Significantly Better
5	Best - Completely Unsoiled

STANDARD OIL TEST LIQUIDS	
Oil-Repellency Rating Number	Composition
1	"Nujol"
2	65/35 "Nujol"/n-hexadecane by volume at 21 ° C
3	n-hexadecane
4	n-tetradecane
5	n-dodecane
6	n-decane

* "Nujol" is the trademark of Plough, Inc., for a mineral oil which has a Saybolt viscosity of 360/390 at 38 ° and a specific gravity of 0.880/0.900 at 15 ° C.

TABLE I

	Air Dried Oil/Water	2 Min. at 200 ° C Oil/Water	2 Min at 200 ° C 5 Home Washings Oil/Water
Comparative Example 1	2/3	0/3	0/0
Comparative Example 2	0/2	6/5	0/4
Example 1	0/3	6/5	6/5
Example 4*	6/5	6/5	6/5
Example 6	0/1	6/5	6/5
Example 7	0/2	6/5	6/5

* Self-dispersing - no surfactant

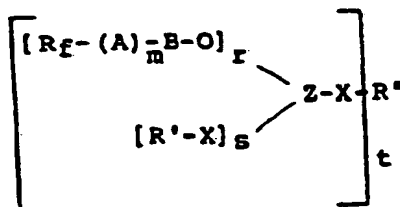
The soil release performance of several of the above exemplified fluorocompounds is tested and compared with an untreated fabric as well as three known soil repellents. The soil repellents are applied to the carpet by padding with the nip rolls set so that after drying 0.075 wt. % of carbon-bonded fluorine remain on the carpet. The carpet used is a standard yellow 30 oz./sq. yard (1.07 Kg/m²) carpet. The results are reported in Table II.

TABLE II

Soil Repellent	Oil Repellency Test	Water Repellency Test	Dry Soil Test	Wet Soil Test
Ex 2	4	5	5	5
Ex 3	2	4	4-5	5-4
Ex 6	4	4-5	5	5
Ex 7	3	5	4-5	5
Commercial Compound A	4	4	2-3	4
Commercial Compound B	2	4	2-3	5-4
Commercial Compound C	2	4	2-3	5
Control (untreated fabric)	0	1	0	0

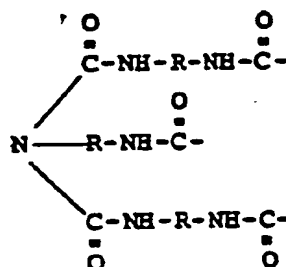
Claims

1. A fluorocarbonylimino biuret of the formula:



wherein

Z is a tris(carbonylimino)biuret radical of the general formula



in which R is an aliphatic or cycloaliphatic residue of 4 to 20 carbon atoms, optionally substituted with alkyl or alkoxy substituents;

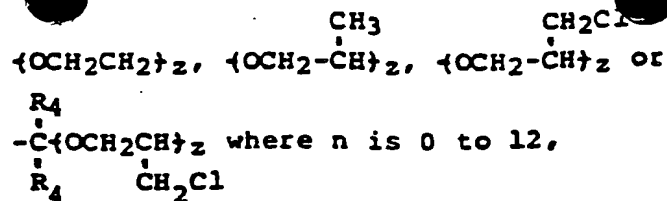
R_f is fully-fluorinated straight or branched aliphatic radical of 3 to 20 carbon atoms which can be interrupted by oxygen atoms;

A is a divalent radical consisting of

-SO₂NR₃-, -CONR₃-,

where R₃ is H or alkyl of 1 to 6 carbon atoms;

B is a divalent linear hydrocarbon radical -C_nH_{2n}- which can be end capped by



z is 1 to 50, and R₄ is H or lower alkyl;

X is O, S or NR₅, where R₅ is H or lower alkyl;

R' is any substituted or unsubstituted fluorine-containing or fluorine-free aliphatic, alicyclic, aromatic or heterocyclic hydrocarbon radical with a valency of at least 2 and not more than 100;

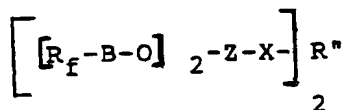
m is zero or 1;

r is 1 or 2;

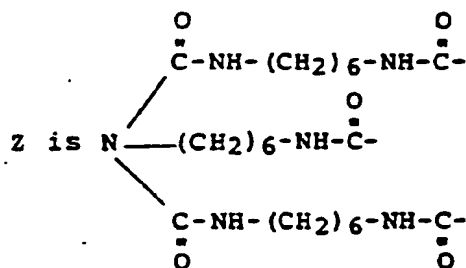
s is (2-r); and

t is an integer of 2 to 100.

2. A fluorocarbonylamino biuret of the formula:



wherein



R_f is -C_nF_{2n+1}, where n is 3 to 14;

B is -C_nH_{2n-}, where n is 2 to 6;

X is O or NH; and

R' is any substituted or unsubstituted fluorine-containing or fluorine-free aliphatic, alicyclic, aromatic or heterocyclic hydrocarbon radical with a valency of 2.

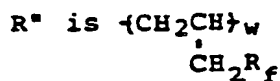
3. A fluorocarbonylimino biuret according to claim 2 wherein

X is oxygen and

R' is -(CH₂)₄-.

4. A fluorocarbonylimino biuret according to claim 2 wherein

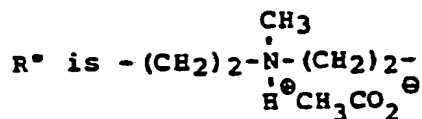
X is oxygen; and



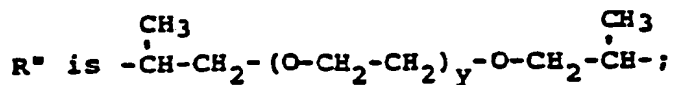
in which R_f is a fluorinated aliphatic radical of at least four fully fluorinated carbon atoms and w is 1 to 4.

5. A fluorocarbonylimino biuret according to claim 2 wherein

X is oxygen and



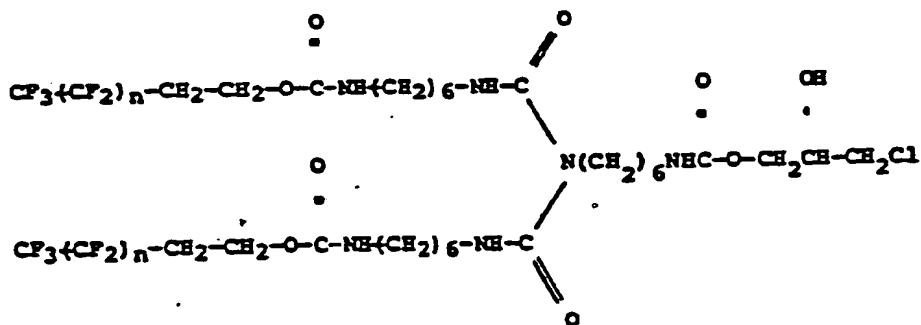
6. A fluorocarbonylimino biuret according to claim 2 wherein



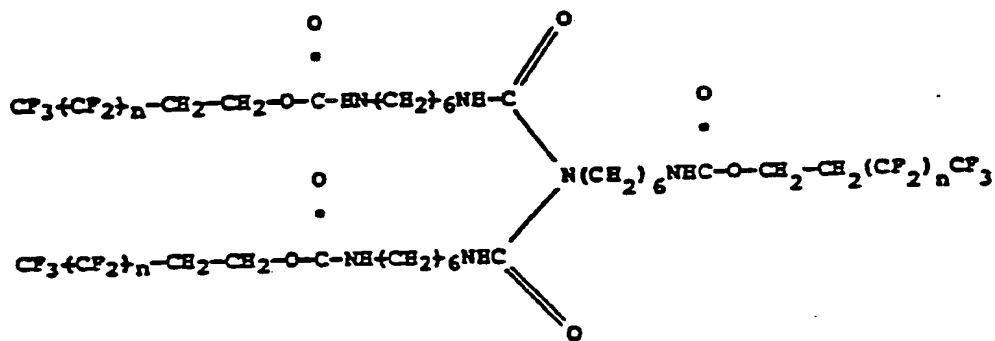
15 X is NH; and

y is 18.

7. A fluorocarbonylimino biuret comprising a mixture of:



and



where n is 3, 4, 5 or mixtures thereof.

8. A synthetic or natural fiber or fabric treated with a fluorocarbonylamino biuret according to any one of the preceding claims to impart oil/water repellency and soil resistance.

9. A nylon or polyester fiber or fabric treated with a fluorocarbonylamino biuret according to any one of the preceding claims to impart oil/water repellency and soil resistance.

10. A nylon or polyester fiber or fabric treated with a blend of a fluorochemical according to any one of the preceding claims and other textile finishing agents to impart oil/water repellency and soil resistance.

6

10

15

20

25

30

35

40

45

50

55

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☒ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.